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# Non-domestic phosphorus release in rivers during low-flow: mechanisms and implications for sources identification

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## **Abstract:**

A common assumption in phosphorus (P) load apportionment studies is that P loads in rivers consist of flow independent point source emissions (mainly from domestic and industrial origins) and flow dependent diffuse source emissions (mainly from agricultural origin). Hence, rivers dominated by point sources will exhibit highest P concentration during low-flow, when flow dilution capacity is minimal, whereas rivers dominated by diffuse sources will exhibit highest P concentration during high-flow, when land-to-river hydrological connectivity is maximal. Here, we show that Soluble Reactive P (SRP) concentrations in three forested catchments free of point sources exhibited seasonal maxima during the summer low-flow period, i.e. a pattern expected in point source dominated areas. A load apportionment model (LAM) is used to show how point sources contribution may have been overestimated in previous studies, because of a biogeochemical process mimicking a point source signal. Almost twenty-two years (March 1995 – September 2016) of monthly monitoring data of SRP, dissolved iron (Fe) and nitrate-N (NO<sub>3</sub>) were used to investigate the underlying mechanisms: SRP and Fe exhibited similar seasonal patterns and opposite to that of NO<sub>3</sub>. We hypothesise that Fe oxyhydroxide reductive dissolution might be the cause of SRP release during the summer period, and that NO<sub>3</sub> might act as a redox buffer, controlling the seasonality of SRP release. We conclude that LAMs may overestimate the contribution of P point sources, especially during the summer low-flow period, when eutrophication risk is maximal.

## **Keywords:**

Soluble reactive phosphorus, iron, redox processes, catchment, point source, load apportionment

## 1. Introduction

Phosphorus (P) concentration in freshwater bodies is an important controlling factor of eutrophication worldwide (Smith and Schindler, 2009). Hence, national and federal regulations, such as the European Water Framework Directive (Directive 2000/60/EC), attach much importance to the reduction of P emissions to streams and rivers. Cost-effective alleviation of P emissions requires precise estimation of the contribution of different P sources in catchments to prioritise management efforts (Bowes et al., 2014; Jarvie et al., 2013b; Withers et al., 2014b).

Point source emissions, mainly from domestic and industrial origins, consist of direct P delivery into the river system. Diffuse source emissions, mainly from agricultural origin, result from the mobilisation of P sources distributed over the landscape and their delivery to rivers (Haygarth et al., 2005). In the case of point source emissions, P delivery from large waste water treatment plants can be monitored directly, but direct assessment of septic tanks leaking in rural areas requires detailed surveys or use of costly fingerprinting techniques (Arnscheidt et al., 2007; Neal et al., 2010; Richards et al., 2016). As an alternative, indirect methods have been developed to determine the relative contribution of point source and diffuse source emissions based on observed concentration-discharge relationships (Bowes et al., 2008, 2014; Greene et al., 2011; Jarvie et al., 2012). These load apportionment models (LAMs) can take different forms, but rely on the same assumptions: point emissions are assumed to be constant in time while diffuse emissions are assumed to increase with discharge, as a result of increasing P mobilisation and delivery during runoff events (Bowes et al., 2015). The point source contribution to P concentration is thus modelled as a linear function of the inverse of discharge (dilution effect) and several equations have been proposed to describe increasing diffuse P concentration during high flow. For example, Bowes et al. (2008) proposed a power function of discharge, and Greene et al. (2011) proposed a linear combination of discharge and the square of discharge. To account for the temporary retention of P during low-flow and its remobilisation during high flow, and not to attribute all the remobilised P to diffuse sources, Jarvie et

al. (2012) proposed an improved version of LAMs using chloride as a conservative tracer of wastewater effluents. In summary, LAMs belong to a large family of empirical models used to fit water quality time series (Minaudo et al., 2017; Moatar et al., 2017; Zhang and Ball, 2017) with the characteristic that they make an explicit distinction between flow dependent and flow independent pollution emissions.

The estimated contribution of point and diffuse sources to annual P loads vary according to the area (Jarvie et al., 2010), but even in catchments where diffuse emissions dominate annual loads, it is common to observe that point source emissions dominate daily P loads during a majority of the time (Greene et al., 2011; Serrano et al., 2015; Sharpley et al., 2009; Shore et al., 2017). Another consequence is that the summer low-flow season is assumed to be dominated by point emissions where they occur and are coincident to known point source pressures (Jordan et al., 2007, 2012; Withers et al., 2014a). Also, because this season is when light and temperature conditions are favourable to eutrophication, river basin managers might decide to target point sources as a priority to mitigate river eutrophication problems in a cost-effective manner (Jarvie et al., 2006; Shore et al., 2017; Stamm et al., 2014).

However, the low-flow period also corresponds to the warm summer season in catchments of the temperate zone, and it is well known that the biogeochemical processes influencing the P cycle in soils and river sediments are temperature dependent (Withers and Jarvie, 2008). In this paper, we hypothesised that temperature dependent biogeochemical processes could lead to P release to rivers during the summer low-flow period and that this release might be unduly attributed to point source emissions in load apportionment studies. To test this hypothesis, three rivers draining small forested catchments free of any point sources were investigated over a 22-year period to: i) quantify the seasonal variability of Soluble Reactive P (SRP) concentration and other solutes, ii) determine if previous P LAMs can be misrepresented by the seasonal dynamics observed, and iii) identify the controlling factors of this seasonal dynamics in order to improve future LAMs.

## 2. Materials and methods

### 2.1. Study area

The Carlsfeld reservoir is located in eastern Germany, in the federal state of Saxony (Figure 1). Its catchment area is 5 km<sup>2</sup> and spans both sides of the German – Czech border. Climate is temperate continental, with mean  $\pm$  standard deviations of annual precipitation and temperature of 1237.0  $\pm$  273.0 mm and 5.7  $\pm$  1.0 °C, respectively (1995 – 2015). Mean monthly temperature varies from -3.0  $\pm$  4.4 °C in January to 14.4  $\pm$  3.8 °C in July (1995 – 2015). The catchment is located in a low-mountain range, the Ore Mountains, with elevations ranging from 904 to 971 m. The geology is dominated by granite capped by podzols (classified as “well drained”) in the upslope domain and organic gleysols (classified as “poorly drained”) in valley-bottoms. Both dominant soil types were classified as “very acidic” (pH < 5), according to the German soil classification (DBK Sachsen, 1:50.000).

Three independent sub-catchments were selected for this study: Carlsfeld 1, 1.8 km<sup>2</sup>; Carlsfeld 2, 0.6 km<sup>2</sup> and Carlsfeld 3, 0.6 km<sup>2</sup> (Figure 1). Their topography is gentle with an average slope of 3° in each of the sub-catchments. The percentage of organic gleysols was 58.2% in Carlsfeld 1, 44.4% in Carlsfeld 2 and 50.2% in Carlsfeld 3. Land use was 100% forest (spruce) without any agriculture or human dwellings. Hence, the three study sub-catchments are free of any point source emissions to the streams and any fertiliser application on the land surface.

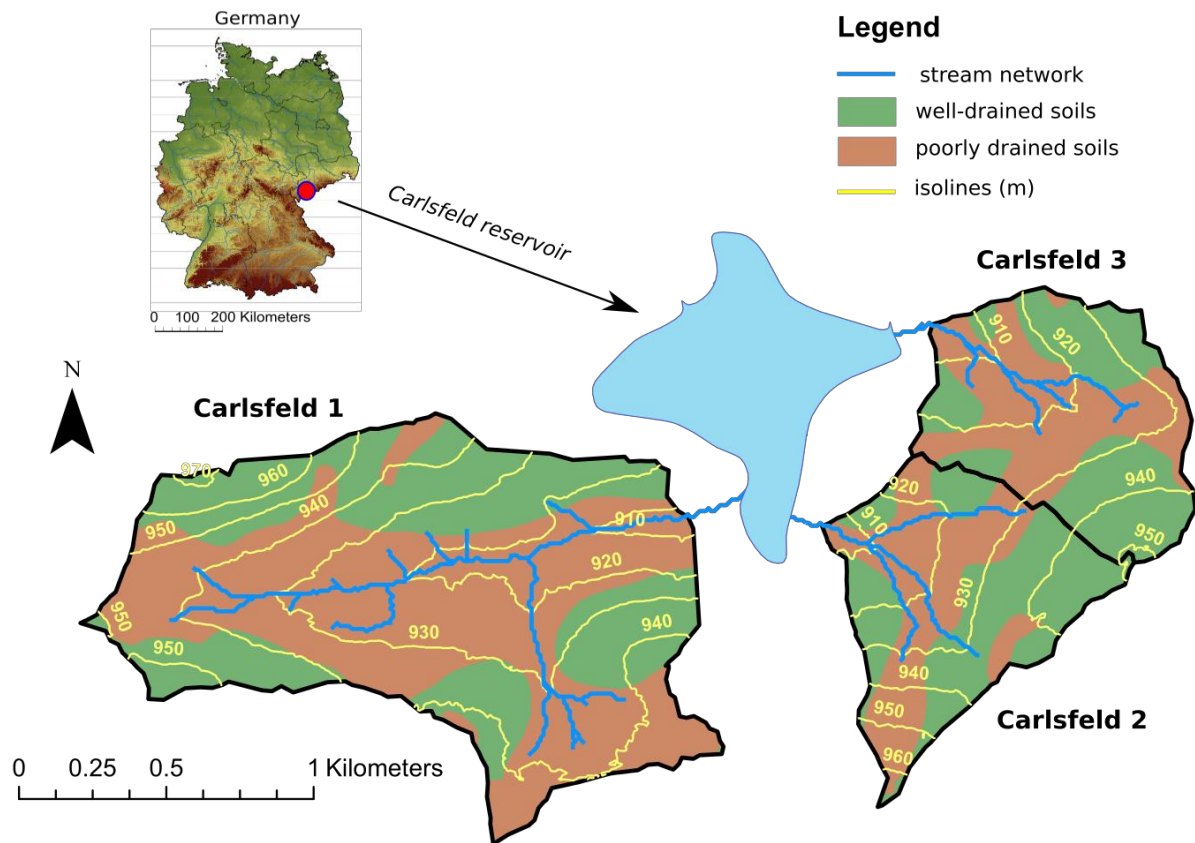


Figure 1: Localisation of the Carlsfeld reservoir and soil types in the three study catchments

## 2.2. Hydro chemical monitoring

The total discharge into the Carlsfeld reservoir was estimated daily from a mass balance calculation involving 15 min record of the reservoir water level (aggregated on a daily basis) and daily record of outflowing discharge. It was assumed that all three sub-catchments had the same specific discharge (in  $\text{mm d}^{-1}$ ), equal to the specific discharge estimated for the whole catchment area of the reservoir. This assumption was considered acceptable because the total catchment area was small, with similar topography and the same land use over the sub-catchments. Discharge data were available for the whole study period (March 1995 to September 2016) except from June 1997 to November 1999 (Figure 2).

Grab samples were collected monthly from March 1995 to September 2016, at the outlet of the three sub-catchments, between 8:00 am and 12:00 pm local time, and analysed for Soluble Reactive Phosphorus (SRP), nitrate-N ( $\text{NO}_3$ ) and dissolved Fe after  $0.45 \mu\text{m}$  filtration (Figure 2). Chemical

analyses of water samples were performed using standard protocols (Wasserchemische Gesellschaft, 2014). SRP was determined colorimetrically by reaction with ammonium molybdate (UV-VIS Specord 200); NO<sub>3</sub> was determined as N by ionic chromatography (ICS-1100 Dionex); Fe was determined by atomic absorption spectrometry (AAS Solaar M5, Thermo).

The three studied catchments have been previously included in two multi-site biogeochemical studies (Musolff et al., 2016; Sucker et al., 2011). A shorter time series of Carlsfeld 1 has also been selected for a showcase analysis of long-term Dissolved Organic Carbon (DOC) and SRP trends in Musolff et al., (2016), and in a DOC load uncertainty evaluation study (Buettner and Tittel, 2013). In contrast to the previously published biogeochemical studies, the present paper focuses on seasonal SRP variations and their implications for LAM.

### **2.3.Data analysis**

The data analysis was threefold.

- The seasonal component of concentration and discharge time series was extracted from a long term trend component using Generalised Additive Models (GAM). GAM are generalized linear models in which the linear form is replaced by a sum of smooth functions (Hastie and Tibshirani, 1987). Technically, the year (1995-2016) and the month (1-12) for each data point were used as predictor variables to estimate the long term non-linear trend and a seasonal component, respectively. The R package *mgcv* (Wood, 2006) was used for this purpose, with cyclic cubic spline to avoid discontinuities at the end points of the spline (in other words, no discontinuity between December and January) and a correction for autocorrelation (autoregressive-moving-average model).
- The significance of trends was quantified by the slope of a linear regression model of annual mean concentration and discharge values as a function of the year. Although the GAM long term trend was not perfectly linear (see results), analysis of residuals showed that a linear model was acceptable to quantify a mean percentage increase or decrease during the study



period and whether this increase or decrease was significant ( $p < 0.05$ ). Only fully monitored years were considered here, i.e. from 1996 to 2015 for concentration data, and 1996 and from 2000 to 2015 for discharge. Percentage exceedance of an indicative SRP eutrophication threshold of  $0.02 \text{ mg SRP l}^{-1}$  (EC, 2002) was estimated for the first ten full years of study (1996-2005) and the last ten full years of study (2006-2015).

- Concentration-discharge (C-Q) plots and concentration-concentration (C-C) plots between each pair of solutes were drawn. A LAM was fitted to the SRP-Q plots, to test whether the observed SRP-Q relationships in catchments without point source emissions could mimic a point source signal. Here the simplest version of the LAM was selected:

$$SRP = \frac{a}{Q} + b * Q^c$$

where  $\frac{a}{Q}$  is the “virtual” contribution of point sources and  $b * Q^c$  is the contribution of diffuse sources. The  $a$  and  $b$  parameters were constrained to be  $>0$  and the  $c$  parameter was constrained to be  $\geq 1$ . A nonlinear least-squares estimate of the parameters was determined with the `nls()` function in the R software (R Development Core Team, 2008). The “virtual” contribution of point sources on annual SRP load and the percentage of the time when “virtual” point sources dominated were estimated separately for the first ten full years of study (1996-2005) and the last ten full years of study (2006-2015). Also for the first ten years and the last ten years of study, alternative empirical (linear) models based on identified SRP controlling factors (see result section 3.2.) were tested and compared. For this comparison the LAM was used without a power law function to allow comparison with other linear models including two parameters.

### 3. Results

#### 3.1. Long term and seasonal variability of SRP, dissolved Fe and nitrate concentrations

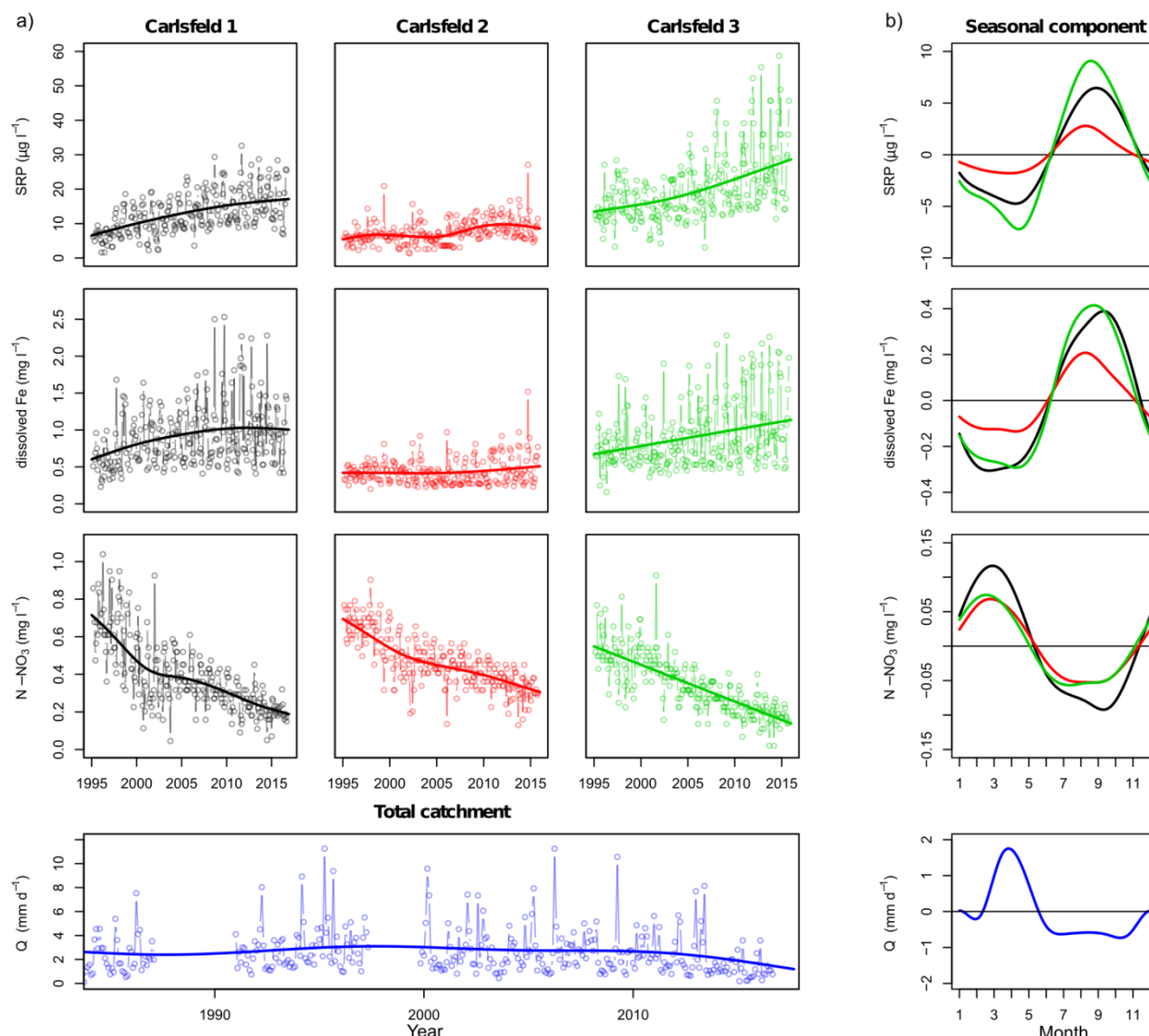
163 Mean ( $\pm$  standard deviation) annual SRP and dissolved Fe concentrations in Carlsfeld 1 ( $13.1 \pm 3.5 \mu\text{g}$   
164  $\text{P l}^{-1}$ ;  $0.92 \pm 0.16 \text{ mg Fe l}^{-1}$ ) and Carlsfeld 3 ( $19.9 \pm 5.3 \mu\text{g P l}^{-1}$ ;  $0.91 \pm 0.17 \text{ mg Fe l}^{-1}$ ) were significantly  
165 higher than in Carlsfeld 2 ( $7.6 \pm 1.8 \mu\text{g P l}^{-1}$ ;  $0.44 \pm 0.07 \text{ mg Fe l}^{-1}$ ) (paired Wilcoxon test,  $p < 0.05$ ,  
166  $n=20$ ). Conversely, mean annual  $\text{NO}_3$  concentration in Carlsfeld 1 ( $0.38 \pm 0.14 \text{ mg N l}^{-1}$ ) and Carlsfeld  
167 3 ( $0.34 \pm 0.12 \text{ mg N l}^{-1}$ ) was significantly lower than in Carlsfeld 2 ( $0.46 \pm 0.11 \text{ mg N l}^{-1}$ ). Differences  
168 between Carlsfeld 1 and Carlsfeld 3 were also significant for SRP and  $\text{NO}_3$  but not for Fe, and the  
169 differences between Carlsfeld 1 and Carlsfeld 3 were generally smaller than between Carlsfeld 1 or 3  
170 and Carlsfeld 2 ( $6.8 \mu\text{g P l}^{-1}$  versus  $5.5$  and  $12.3 \mu\text{g P l}^{-1}$ ,  $0.01 \text{ mg Fe l}^{-1}$  versus  $0.48$  and  $0.47 \text{ mg Fe l}^{-1}$ ,  
171  $0.04 \text{ mg N l}^{-1}$  versus  $0.08$  and  $0.12 \text{ mg N l}^{-1}$ , respectively).

172 From 1996 to 2015, mean annual SRP concentration increased significantly (linear model,  $p < 0.05$ ,  
173  $n=20$ ) in the three catchments ( $+121\%$  in Carlsfeld 1,  $+72\%$  in Carlsfeld 2 and  $+106\%$  in Carlsfeld 3).  
174 In Carlsfeld 1 and Carlsfeld 3, significant increases in the mean annual concentration of dissolved Fe  
175 ( $+47\%$  and  $+62\%$ , respectively) were also observed, but not in Carlsfeld 2 ( $p > 0.05$ ). Conversely,  
176 mean annual  $\text{NO}_3$  concentration decreased significantly in the three catchments ( $-66\%$  in Carlsfeld 1,  
177  $-48\%$  in Carlsfeld 2 and  $-67\%$  in Carlsfeld 3). No trend in mean annual discharge, precipitation or  
178 temperature could be detected from 1996 to 2015 (Figure S1), although the discharge long term  
179 trend appeared to decrease between 2012 and 2016 (Figure 2a).

180 Similar to the long-term trend, the seasonal dynamics of SRP and dissolved Fe mirrored that of  $\text{NO}_3$   
181 (and discharge) in the three catchments: SRP and dissolved Fe reached their seasonal maximum in  
182 the late summer (August to October) which corresponded to the period with the lowest  $\text{NO}_3$   
183 concentration and the lowest discharge (Figure 2b). Conversely,  $\text{NO}_3$  reached its seasonal maximum  
184 during the high flow period (March to May). The SRP and dissolved Fe seasonal dynamics and trends  
185 also seemed to be dependent on  $\text{NO}_3$  values and  $\text{NO}_3$  decreasing trends: in Carlsfeld 2, where  $\text{NO}_3$   
186 concentrations were the highest and  $\text{NO}_3$  decreasing trend was the lowest, the seasonal amplitude

187 of the dissolved Fe and SRP signal was weaker than in Carlsfeld 1 and 3, where NO<sub>3</sub> concentrations  
188 were lower and NO<sub>3</sub> decreasing trends were stronger (Figure 2).

189 The number of months for which SRP concentration exceeded the indicative eutrophication  
190 threshold of 0.02 mg l<sup>-1</sup> increased for two of the three study catchments, between the first ten full  
191 years of record (1996-2005) and the last ten full years of record (2006-2015). In Carlsfeld 1, this  
192 threshold was exceeded 3% of the time during the first period and 24% of the time during the second  
193 period. In Carlsfeld 3, the threshold was exceeded 26% of the time during the first period and 53% of  
194 the time during the second period. In Carlsfeld 2, exceedance represented less than 0.1% of the time  
195 during both periods. The season at which this exceedance was observed in Carlsfeld 1 and 3 was  
196 mainly the late summer period (Figure 2), i.e., a period where light and temperature conditions are  
197 favourable for eutrophication.



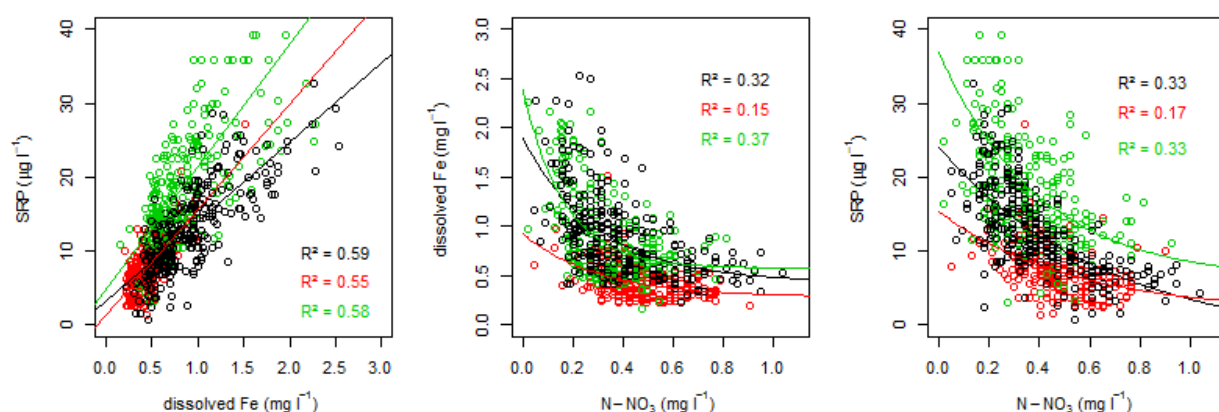
**Figure 2: Monthly concentration and discharge data and long term components of GAM model (a) and seasonal component of GAM model (b). Open circles represent the original monthly time series and bold lines represent long term (a) and seasonal (b) GAM components.**

### 3.2.C-Q and C-C relationships

None of the three solutes studied exhibited a clear and univocal relationship with discharge for the entire study period (1995-2016). Nitrate concentration was not significantly correlated with discharge ( $p > 0.1$ ) and SRP and dissolved Fe exhibited high concentrations both for the lowest and the highest discharge values (Figure S2). This lack of a clear relationship between concentrations and discharge is in apparent contradiction with the seasonal GAM component (Figure 2b), which shows that NO<sub>3</sub> dynamics were in phase with discharge while SRP and dissolved Fe had opposite seasonal

dynamics to discharge. However, the solutes were affected by large long term trends, and this was not the case for discharge; consequently, the C-Q relationships changed from year to year and these relationships taken for the entire study period could not exhibit clear patterns.

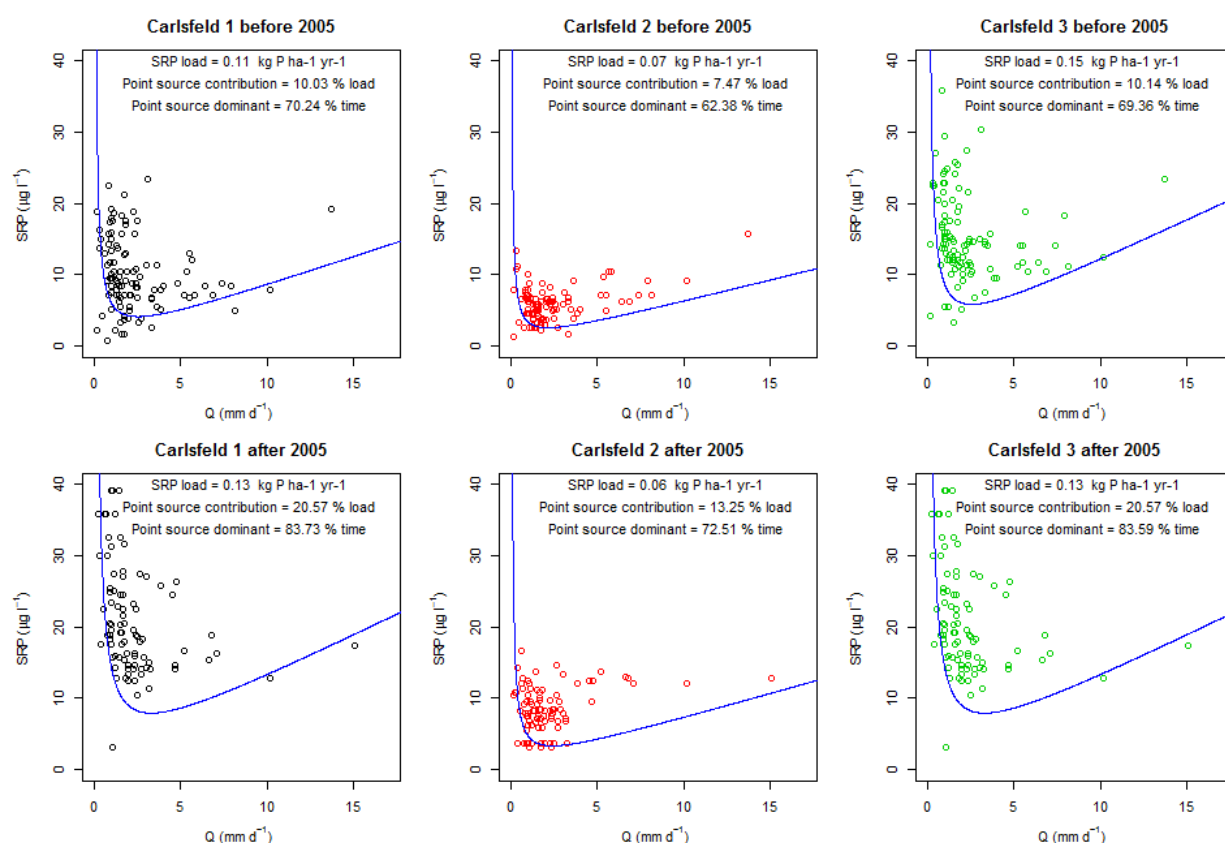
Contrary to the C-Q plots, the C-C plot showed clear relationships between pairs of solutes (Figure 3), for the entire study period (1995-2016). Soluble reactive P was significantly ( $p < 0.05$ ) correlated with Fe ( $r = 0.74 - 77$ ), and both SRP and Fe exhibited a similar non-linear decreasing relationship with  $\text{NO}_3$ , fitted with an exponential function in Figure 3.



**Figure 3: Concentration-concentration relationships between pairs of solutes. The relationship between SRP and dissolved iron was fitted with a linear model  $y = a + b \cdot x$ , and the relationship between  $\text{NO}_3$  and dissolved Fe and between  $\text{NO}_3$  and SRP was fitted with an exponential model  $y = a + b \cdot \exp(-c \cdot x)$ . Carlsfeld 1 in black, Carlsfeld 2 in red, Carlsfeld 3 in green.**

According to the SRP-Q LAM (Figure 4), annual loads varied from 0.06 to 0.15 kg SRP  $\text{ha}^{-1} \text{yr}^{-1}$  for all three catchments and for the two periods considered: prior to 2005 and after 2005. The differences between catchments reflected their different SRP concentrations visible in Figure 2, as specific discharge was assumed to be the same. Estimated loads were similar before and after 2005, but this result must be considered with care as the load estimation method is very sensitive (by construction) to the high flow data points, and the number of these may differ between the two periods. Therefore, it would not be reasonable to split the 22 years into more than two periods to apply the LAM, as these models are very sensitive to the monitoring frequency and/or duration (Crockford et

al., 2017). More interestingly, the estimated virtual contribution of point sources increased in the three sub-catchments. In Carlsfeld 1, the virtual contribution of point sources increased from 10% to 21% between the first ten years of study (1996-2005) and the last ten years (2006-2015), and this virtual point sources contribution dominated daily loads during 70% and 84% of the time during the two periods, respectively. In Carlsfeld 2, the virtual contribution of point sources increased from 7% to 13%, and this virtual point sources contribution dominated daily loads during 62% and 73% of the time during the two periods, respectively. In Carlsfeld 3, the virtual contribution of point sources increased from 10% to 21%, and this virtual point source contribution dominated daily loads during 70% and 84% of the time during the two periods, respectively. By construction, the model predicted point sources to dominate during the low-flow period, i.e., the late summer period (Figure 2), which is also the period at highest eutrophication risk due to optimal light and temperature conditions.



**Figure 4: Result of the concentration-discharge load apportionment model (blue line) in the three study catchments and for two periods (before and after 2005).**

Five alternative empirical models were compared for their capacity to fit the SRP data. Simple linear regressions including discharge or the inverse of discharge all performed poorly, with  $R^2$  close to 0 (Table 1). The LAM performed fairly well with two variables ( $R^2 = 0.57 - 0.79$ ) but the performance of the “biogeochemical model” (Table 1) was almost as high with only dissolved Fe as a predictor variable ( $R^2 = 0.37 - 0.64$ ). The fitted parameters with this equation were:

$$\text{Carlsfeld1 (before 2005): } SRP = 1.4 * 10^{-3} + 1.1 * 10^{-2} * Fe$$

$$\text{Carlsfeld1 (after 2005): } SRP = 6.1 * 10^{-3} + 9.1 * 10^{-3} * Fe$$

$$\text{Carlsfeld2 (before 2005): } SRP = 1.1 * 10^{-3} + 1.2 * 10^{-2} * Fe$$

$$\text{Carlsfeld2 (after 2005): } SRP = 3.0 * 10^{-3} + 1.3 * 10^{-2} * Fe$$

$$\text{Carlsfeld3 (before 2005): } SRP = 5.6 * 10^{-3} + 1.3 * 10^{-2} * Fe$$

$$\text{Carlsfeld3 (after 2005): } SRP = 7.4 * 10^{-3} + 1.5 * 10^{-2} * Fe$$

With SRP and Fe in  $\text{mg.l}^{-1}$  and Q in  $\text{mm.d}^{-1}$ .

The best model with two variables was the “biogeochemical model” + discharge ( $R^2 = 0.92 - 0.93$ ), in which the part of the equation corresponding to the dilution of a constant source in the LAM is replaced by a linear function of dissolved Fe.

**Table 1: Comparison of the coefficient of determination  $R^2$  for five linear models fitted to the first ten years of study (1996 - 2005) and the last ten years (2006-2015) of study in the Carsfeld sub-catchments.**

<u>model</u> <u>description</u>	<u>model equation</u>	R <sup>2</sup> Carlsfeld 1		R <sup>2</sup> Carlsfeld 2		R <sup>2</sup> Carlsfeld 3	
		before 2005	after 2005	before 2005	after 2005	before 2005	after 2005
Dilution of a constant source	SRP ~ 1/Q + intercept	0.02	0.05	0.00	0.01	0.01	0.22

Increasing export with discharge	SRP ~ Q + intercept	0.01	0.01	0.14	0.04	0.01	0.03
Load apportionmen t model	SRP ~ 1/Q + Q	0.64	0.57	0.79	0.58	0.66	0.62
"Biogeochemi cal model"	SRP ~ Fe + intercept	0.59	0.64	0.37	0.57	0.47	0.56
"Biogeochemi cal model" + increasing export with discharge	SRP ~ Fe + Q	0.92	0.93	0.93	0.93	0.93	0.92

## 4. Discussion

A recent study of SRP and DOC trends in 110 German catchments draining into drinking water reservoirs (including the 3 Carlsfeld sub-catchments) has documented a long term increase in SRP and DOC, associated with an increase in dissolved Fe and a decrease in NO<sub>3</sub> in catchments with acidic soils (Musolff et al., 2016). The authors concluded that Fe oxyhydroxide reduction was the dominant mechanism explaining increased SRP and DOC release into streams and that NO<sub>3</sub>, being a stronger electron acceptor than Fe, acted as a redox buffer. According to this hypothesis, decreasing atmospheric N deposition could lead to a decrease in NO<sub>3</sub> redox buffering capacity and this decrease is the main cause of the observed increasing SRP and DOC trends in these catchments. Our trend observations are compatible with the redox hypothesis, hence long term trends in the Carlsfeld sub-catchment will not be discussed further in this paper. Rather, in section 4.1. we discuss whether the redox hypothesis and NO<sub>3</sub> redox buffering could also explain the seasonal variability in SRP observed



in the Carlsfeld sub-catchments. Also, in section 4.2., we discuss the implications of the observed SRP seasonal dynamics in terms of water quality assessment and management.

#### **4.1. Interplay of hydrological and biogeochemical processes**

Previous studies have demonstrated that variability in dominant flow pathways or in the contribution of several conceptual compartments with different chemical signatures exert a large control on SRP and NO<sub>3</sub> concentrations in rivers (Mellander et al., 2012; Dupas et al., 2017a), and that this variability is influenced by changing hydroclimatic conditions on a seasonal or inter annual basis (Ockenden et al., 2016). In catchments with similar shallow groundwater systems and presence of riparian wetlands, the seasonal variability of SRP and NO<sub>3</sub> has previously been explained by the high contribution of a riparian compartment (rich in SRP due to the shallow groundwater interacting with the organic soils and poor in NO<sub>3</sub> due to denitrifying conditions) during the dry season, and by the high contribution of an upslope compartment (poor in SRP due to the deeper groundwater and richer in NO<sub>3</sub> because of limited denitrification in well-drained soils) during the wet season (Dupas et al., 2016, 2017a; Exner-Kittridge et al., 2016; Martin et al., 2004; Woodward et al., 2013). Here, the fact that the two sub-catchments with substantially higher SRP concentrations, and lower NO<sub>3</sub> concentration (Carlsfeld 1 and 3), are also those with the highest percentage of organic riparian soils (see section 2.1), supports previous assertions that organic riparian soils are internal sources of SRP (Dupas et al., 2017b; Gu et al., 2017; Records et al., 2016), and a buffer zone for NO<sub>3</sub> (Anderson et al., 2014; Oehler et al., 2009). Other factors such as P speciation in soils may also play a role (Gu et al., 2017). However, a conceptual model relying only on the hydrological connectivity of two conceptual compartments with different chemical signatures is questionable, as all water flows pass through the riparian wetland and/or hyporheic zone and should, according to this conceptual model, lose NO<sub>3</sub> through denitrification and gain SRP through interactions with organic soils regardless of the season. In this respect, the question of water residence time and temperature is crucial, in conjunction with an interpretation based on the mixing of conceptual compartments (Hrachowitz et al., 2016; Pinay et al., 2015). In the Carlsfeld sub-catchments, residence times in the riparian

compartment were arguably too short during the wet period, when groundwater hydraulic gradients are maximal and flow velocity at their highest, and temperatures too low, for denitrification and SRP solubilisation to take place. The central role played by biogeochemical processes in SRP release mechanisms is illustrated by the C-C relationships (Figure 3) which, contrarily to the C-Q plots (Figure S2), appeared to be stable in the long term. The strong correlation between SRP and dissolved Fe, and the negative relationships between SRP or dissolved Fe with NO<sub>3</sub> support the hypothesis of a dominant redox control on seasonal SRP release during the summer period (Li et al., 2012; Musolff et al., 2016; Smolders et al., 2017). Furthermore, sulphate concentrations and pH do not exhibit seasonal cycles in these catchments (Figure S3). Simultaneous release of ferrous Fe and SRP have been measured in-situ in riparian soils (Dupas et al., 2015; Gu et al., 2017; Surridge et al., 2007; van der Grift et al., 2014), and the same authors observed that NO<sub>3</sub> could play the role of a redox buffer that determines the timing of Fe oxyhydroxides reductive dissolution and subsequent SRP release. Hence, the seasonal variability of NO<sub>3</sub> inputs to the riparian wetland, with high inputs from the upslope nitrate rich compartment during the wet period and lower inputs combined with higher denitrification during the warmer summer period (Dupas et al., 2016; Exner-Kittridge et al., 2016; Woodward et al., 2013), could govern SRP seasonal dynamics via reductive desorption of SRP previously bound to Fe oxyhydroxides. Hydrology is both a proximate and ultimate control (e.g. Thomas et al., 2016) of the seasonal variability in SRP and NO<sub>3</sub> in the streams of the Carlsfeld catchment.

The hypothesis of a dominant redox control on SRP and dissolved Fe dynamics is apparently contradicted by field observation in intensively farmed regions of Belgium and the Netherlands that phosphate and Fe oxyhydroxides usually co-precipitate during exfiltration of anoxic groundwater to oxic stream waters, and thus phosphate is retained within soils and sediments (Baken et al., 2015; van der Grift et al., 2014). However, Baken et al. (2016) have shown in the same region that in-stream water with a P:Fe molar ratio below 0.1, co-precipitation of phosphate and Fe oxyhydroxides was not leading to retention but instead could form mobile Fe-rich colloids which can be transferred

to the streams. The mean and maximum P:Fe molar ratio in the three Carlsfeld sub-catchments ranged from 0.03 to 0.04 and 0.06 to 0.12 respectively, i.e. below or close to the threshold proposed by Baken et al. (2016). This means that with the relatively low SRP concentrations observed in the Carlsfeld sub-catchments, it is likely that Fe-rich colloids are the vector of P, and that these Fe-P colloids can still be measured as SRP (Gu et al., 2017; Sinaj et al., 1998; Van Moorlegghem et al., 2011).

To conclude, a biogeochemical process releasing SRP during the summer period was identified: both a temperature control and a hydrological control, via residence times and NO<sub>3</sub> influx to the riparian reactive zone, and are likely to explain the seasonal dynamics observed.

#### **4.2.Implications for water quality assessment and management**

The observed SRP dynamics has implications for water quality assessment. LAMs based on C-Q relationships might overestimate point source contributions in some contexts where there is a presence of point sources (i.e. the contexts where load apportionment models can usually be used), because a biogeochemical process releasing SRP during summer low-flow can augment the point source signal. This summer SRP release, exceeding 0.05 mg l<sup>-1</sup> in one of the study catchments, is likely to have a significant impact on LAMs in many contexts where small point sources occur: for example in the TERENO Harz/Central German Lowland Observatory, a 3300 km<sup>2</sup> area encompassing large gradients of land use and elevation in Central Germany and including small point sources, summer SRP concentrations range from < 0.01 mg l<sup>-1</sup> to 0.12 mg l<sup>-1</sup> (Kamjunke et al., 2013). Therefore, we recommend combining these C-Q LAMs with markers of effluent discharge and survey of point emissions, at least to test the method in catchments where point emissions are well identified and quantified (Arnscheidt et al., 2007; Neal et al., 2010; Richards et al., 2016). Error in source identification will have an impact on the cost-effectiveness of measures to remediate P in rivers because managers might choose to target point sources as a priority, whereas diffuse source contribution during the summer growing season might be larger than previously estimated (Jarvie et

al., 2006, 2013b; Withers et al., 2014a, 2014b). In addition, evaluation of water quality remediation programmes targeting reduction of P inputs on agricultural land might be misled by the long term SRP trend, controlled by processes independent from inputs, which could mask the effect of improved management practices within catchments.

Although the seasonal SRP dynamics can mimic a point source signal, as highlighted by the relatively good fit of the LAM, a better fit to the data was obtained with an empirical model including dissolved Fe as a predictor variable. However, the latter cannot be transferred to catchments where both the summer SRP release from riparian wetlands and point source emissions take place, because the dissolved Fe – SRP relationship established for the Carlsfeld sub-catchment will probably not be valid in other areas. It would, therefore, be necessary for further research to determine the controlling factor(s) of this dissolved Fe – SRP relationship (e.g. soil Fe and P content and speciation, hydrology, land use), as it could provide a basis for a new generation of LAMs that disentangle summer SRP release from riparian wetlands and point source emissions.

The observed SRP dynamics has implications for water quality management, because management options generally do not take into account the interactions between nitrogen and phosphorus. If the hypothesis of NO<sub>3</sub> buffering SRP release is confirmed in catchments with higher anthropogenic pressures, remediation programmes targeting N as a priority might result in increasing SRP concentrations in streams and rivers. Even when both N and P are targeted by remediation programmes, the long term legacy of P in soils (Jarvie et al., 2013a) might lead to a slow depletion of the P accumulated in the catchment as compared to N, thus increased SRP release from riparian wetlands (in summer) is possible.

Further research is needed to determine if the hypothesis of NO<sub>3</sub> buffering SRP release, followed by SRP delivery to streams, can take place also in agricultural catchments, where N inputs are much higher than in the study case presented here. The comparison of the three Carlsfeld sub-catchments suggests that redox mediated SRP release needs extremely low NO<sub>3</sub> concentration to take place: in

Carlsfeld 2, where SRP release seemed to be almost inhibited compared to Carlsfeld 1 and 3, the mean annual NO<sub>3</sub> concentration was only  $0.46 \pm 0.11 \text{ mg N l}^{-1}$ , a concentration far below what is commonly measured in agricultural areas. However, redox mediated SRP release has been documented in some of the regions with the highest agricultural pressures in Europe such as Western France (Dupas et al., 2015; Gu et al., 2017), Belgium (Baken et al., 2016) and the Netherlands (van der Grift et al., 2014). Hence stream nitrate NO<sub>3</sub> may not in isolation be a good indicator of redox mediated SRP release, as this process can take place in local organic rich hotspots where NO<sub>3</sub> is absent, whereas in agricultural areas NO<sub>3</sub> can still be high in deeper flow paths.

## 5. Conclusions

In this study, with direct implications for catchment management and monitoring programmes where eutrophication is an issue, we showed that:

- a biogeochemical process releasing SRP during summer low-flow can mimic a point source signal and may lead to overestimation of point source contributions in P load apportionment studies;
- a long term increasing SRP trend could possibly mask the effect of reduced P inputs in some areas;
- seasonal reductive dissolution of Fe oxyhydroxides is a probable mechanism for the summer SRP release from riparian wetland soils, under the control of temperature, residence times and NO<sub>3</sub> influx.

Further methodological developments are necessary to include summer SRP release from riparian wetlands into LAMs, especially in rural areas where domestic P emissions are difficult to evaluate due to their scattered distribution throughout catchments.

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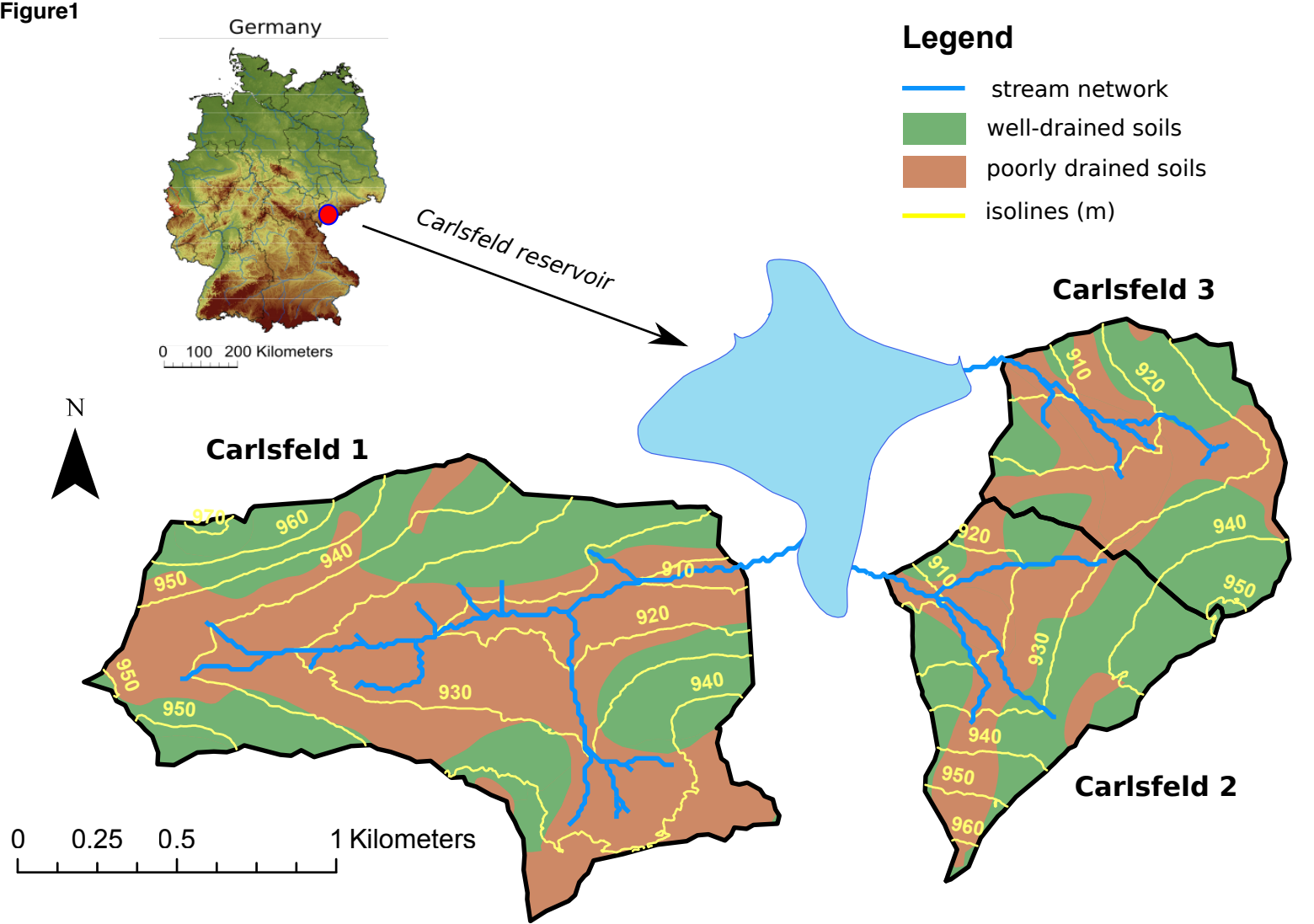
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Figure1



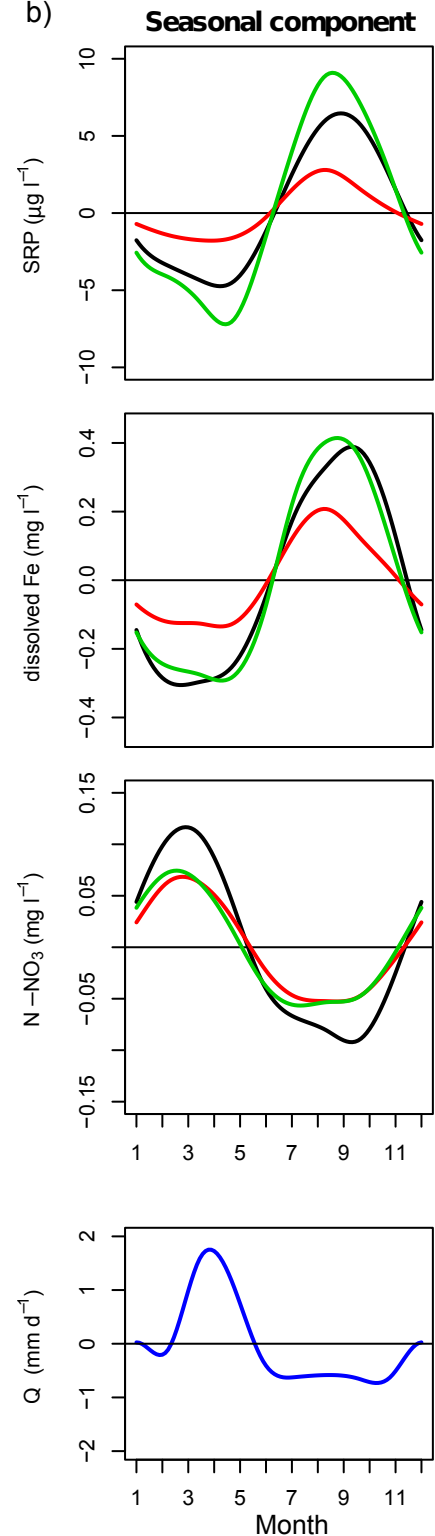
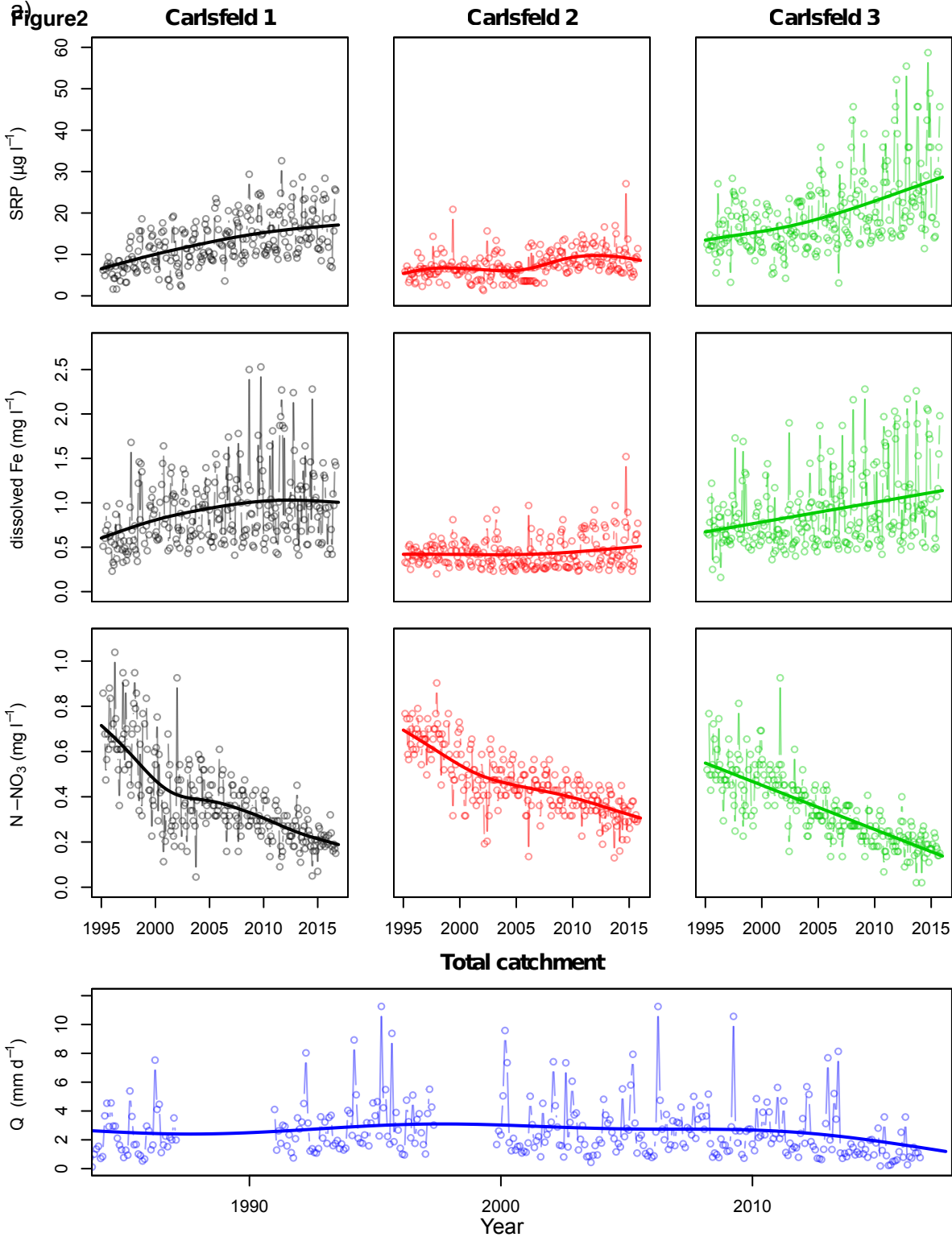
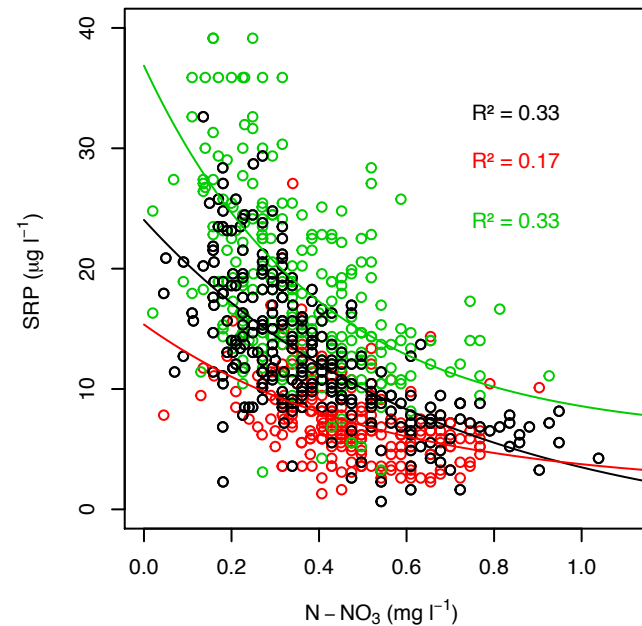
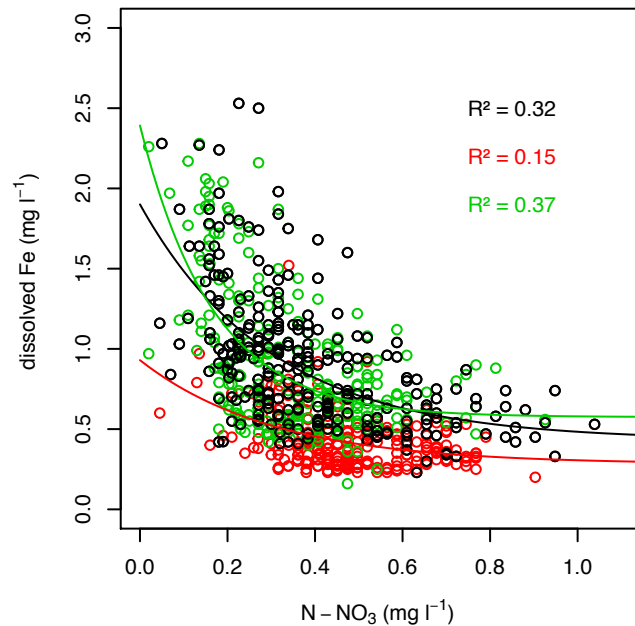
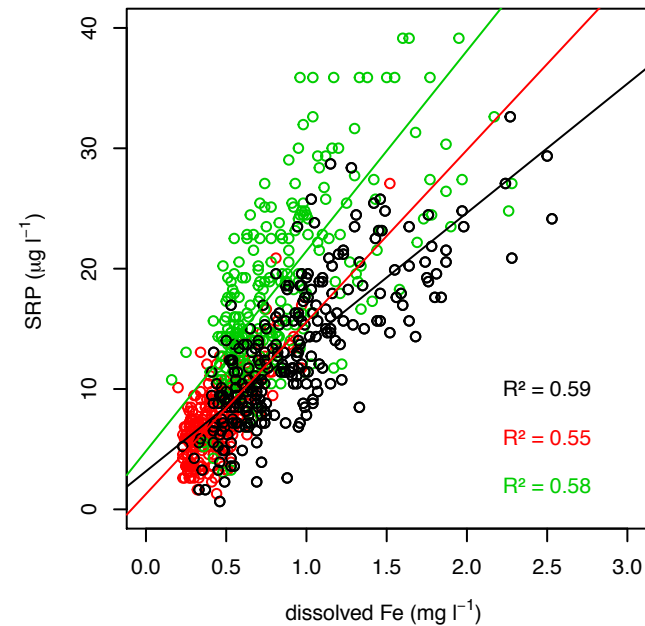
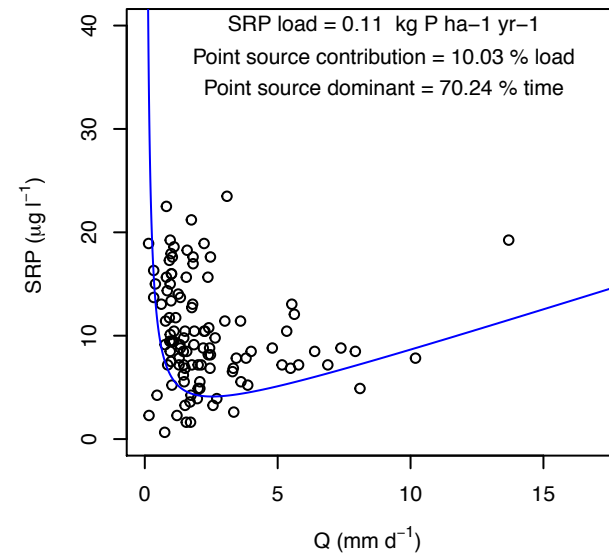
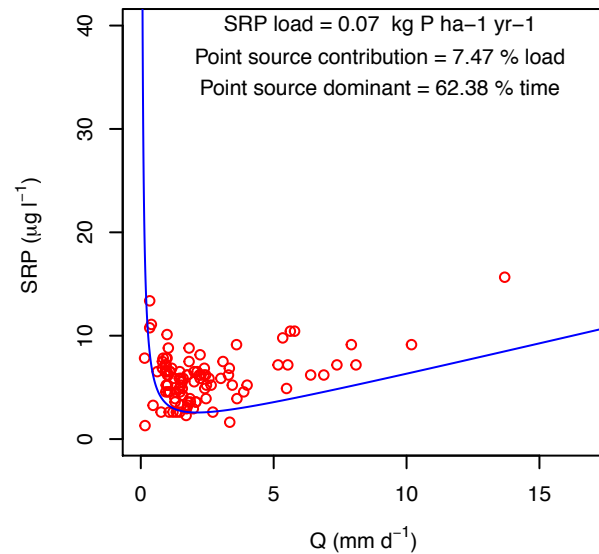
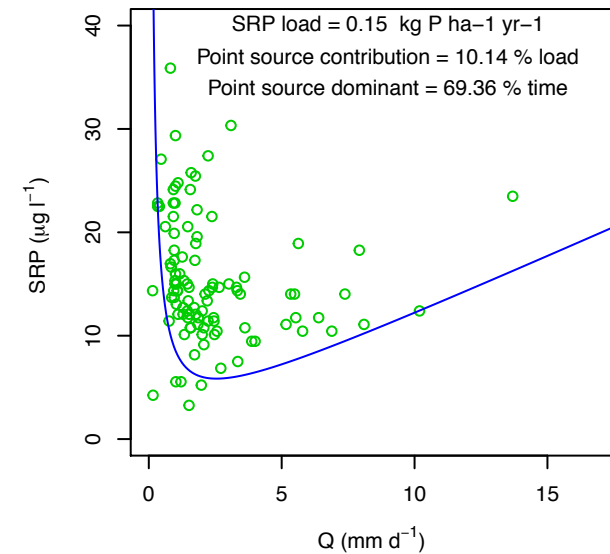
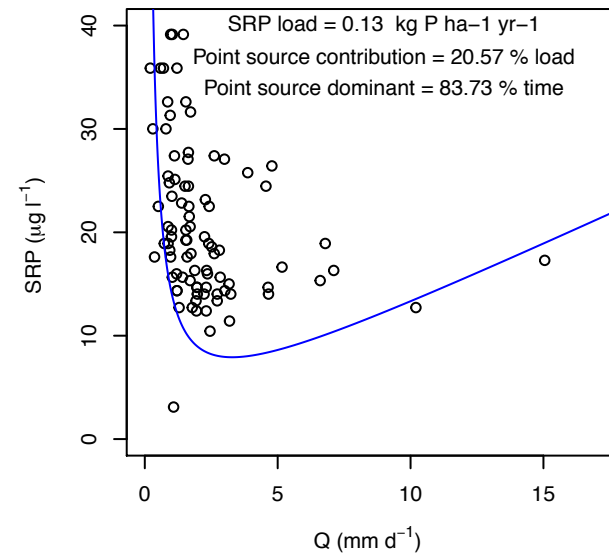
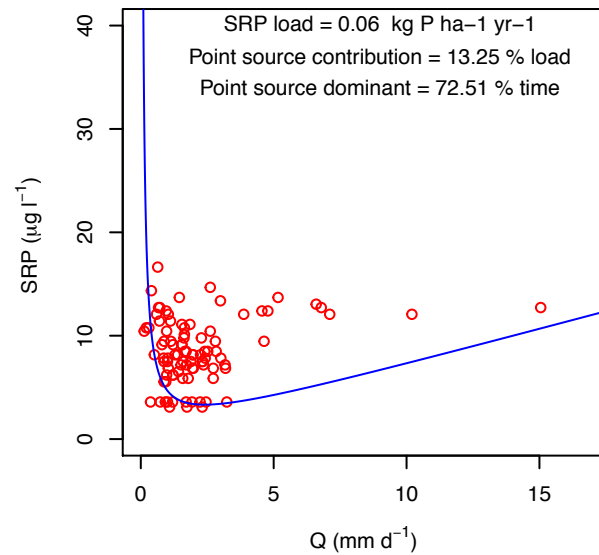
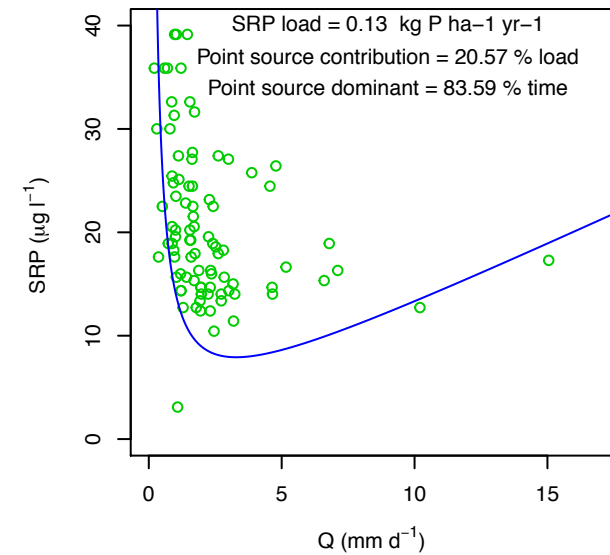


Figure3



**Figure4****Carlsfeld 1 before 2005****Carlsfeld 2 before 2005****Carlsfeld 3 before 2005****Carlsfeld 1 after 2005****Carlsfeld 2 after 2005****Carlsfeld 3 after 2005**

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